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LOW-COST SOLAR ARRAY PROJECT

TASK I SILICON MATERIAL

"Investigation of the Hydrogenation of $SiCl_4$"

QUARTERLY REPORT

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CONTRACT NO. 955382

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ABSTRACT

A program was initiated in April of this year to study the hydrogenation of silicon tetrachloride to trichlorosilane,

$$3\ SiCl_4 + 2\ H_2 + Si \rightleftharpoons 4\ SiHCl_3$$

This Contract is conducted as a complementary research and development program to supplement the engineering process development activities for the process-unit under Union Carbide Contract No. 954 334. Two parallel efforts are included in the submitted Program Plan. One is a process study to collect reaction kinetic data on the rate of the hydrogenation reaction as a function of various reaction parameters. The other is a basic research effort to study the reaction mechanism and to develop new catalysts to improve the reaction rate and the conversion of $SiCl_4$ to $SiHCl_3$.

A laboratory stainless steel reactor is designed to operate at pressures up to 500 psig and reactor temperatures up to 600°C. Construction of the hydrogenation apparatus has progressed according to the Program Plan. An in-line gas chromatograph is built onto the reactor assembly to provide accurate, instantaneous analysis of the reaction product mixture. The hydrogenation apparatus is also semi-automated so that it can be run continuously. This design feature is especially useful for prolonged reactions to study the life of the Si mass bed. Start-up of the hydrogenation reactor is scheduled for the month of August.

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INTRODUCTION

Work on the JPL Government Contract No. 955 382 began in April of this year to study the hydrogenation of $SiCl_4$ to $SiHCl_3$. This complementary research and development effort is conducted to supplement the engineering process development activities for the process-unit under the Union Carbide Contract No. 954 334. The hydrogenation of $SiCl_4$ produces $SiHCl_3$,

$$3\ SiCl_4 + 2\ H_2 + Si \rightleftharpoons 4\ SiHCl_3$$

The product, $SiHCl_3$, is the starting material for the production of silane, SiH_4, in the Union Carbide silane-to-silicon process. This reaction step is critical since approximately 100 lbs of $SiCl_4$ is processed up-stream in order to produce 1 lb of SiH_4 down-stream. A significant improvement of this hydrogenation step will benefit the overall economics of the silane-to-silicon process.

DISCUSSION

A. Program Plan

The attached Program Plan summarizes the activities on the investigation of the hydrogenation of $SiCl_4$. A laboratory-scale pressure reactor will be constructed within the first five months of the Contract. Then two parallel efforts, V, Process Studies, and VI, Research and Development, will be implemented. The process studies are designed to collect reaction kinetic data as a function of temperature, pressure, $H_2/SiCl_4$ ratio,

copper catalyst concentration, surface area and the effect of impurities in the metallurgical grade silicon metal, etc. The effect of prolonged reaction on the rate of the hydrogenation of $SiCl_4$ to $SiHCl_3$ will be studied in order to establish the life of the Si mass bed. These mass life studies also will provide reaction kinetic data as a function of catalyst balance, accumulation of heavy metal halides, elutriation of fines, segregations, etc. On the other hand, the Research and Development, VI, in the Program Plan is a comprehensive study on the mechanism of the hydrogenation reaction to provide a basic understanding of this process. Also included in this Research and Development effort is the development of new catalyst systems and new technologies to improve the reaction rate and the conversion of $SiCl_4$ to $SiHCl_3$. Finally, recommendations will be made to JPL at various check points on the optimum reaction conditions for carrying out the hydrogenation process and on areas for additional development work.

B. The Hydrogenation Apparatus

The hydrogenation reactor design is shown schematically in Figure I (attached). The operating principles are as follows. A constant flow of hydrogen gas from a cylinder is metered through a fine needle valve. The gas flow-rate is measured by a mass flowmeter. The hydrogen gas is dispersed into a liquid column of $SiCl_4$ contained in a stainless steel cylinder. The $SiCl_4$ liquid is heated by circulating a heat transfer fluid from a constant temperature bath through the condenser jacket on the

stainless steel cylinder. The molar ratio of $H_2/SiCl_4$ can be conviently selected by adjusting the temperature of the $SiCl_4$ liquid and by the applied hydrogen pressure. The gaseous $H_2/SiCl_4$ mixture then is fed into the one-inch inside diameter fluidized-bed reactor containing the Si metal. The reaction product mixture coming out of the reactor is analyzed by the in-line gas chromatograph which is directly built onto the reactor assembly. This in-line arrangement provides accurate, instantaneous analysis of the total product composition. These measurements will provide data for the reaction kinetics as a function of various reaction parameters. The chlorosilane vapor is condensed by the -65°C condenser as shown in Figure I. Cooling to the -65°C condenser is accomplished by circulating a heat transfer fluid thorugh the condenser jacket from a Dry-Ice bath. The chlorosilane liquid product mixture is collected in a stainless steel receiver and can be withdrawn out of the hydrogenation apparatus. The weight of the chlorosilane products and the weight of the spent Si mass provide data to check the mass balance of the hydrogenation process.

1. Special Design Features

The rate of the hydrogenation reaction has been shown to be very much dependent on the reactor temperature. Thus, the fluidized-bed reactor is carefully designed to assure that uniform reactor temperatures can be controlled precisely and that they are reproducible. The 1-1/4 inch diameter reactor tube is electrically heated. In addition to the main heater

which controls the reactor temperature through a thermo couple temperature controller, there are four sectional heaters placed along the reactor tube. These sectional heaters can be individually adjusted so as to compensate for the different degree of heat loss along the reactor tube, especially at the ends of the reactor. Design of the reactor inlet and the grid is shown in Figure II. A stainless steel block is machined to the shape as shown in Figure II and placed at the inlet of the reactor tube. The stainless steel block raises the Si mass bed about six inches above the bottom end of the reactor tube. The Si mass bed is now totally enclosed by the electric heaters. A uniform temperature profile along the reactor tube can be achieved by fine tuning the individual electrical heaters. The heavy stainless steel block provides good transfer of heat to the bottom end of the reactor tube. Also, the uniform temperature along the stainless steel block helps to adjust the inlet $H_2/SiCl_4$ gas temperature close to the reactor temperature. The $H_2/SiCl_4$ gaseous mixture is dispersed into the Si mass bed through a grid. The reactor grid is a 5-orifice design as shown in Figure II. This design was selected from several variations by experimenting with a fluidized mass bed of Si metal with nitrogen gas in one inch-diameter glass tubing. The quality of fluidization is judged visually. The 5-orifice grid design appears to give the best results.

An inlet port is provided at the hydrogenation reactor to charge fresh Si metal, copper catalyst and other material into the Si mass bed. This Si metal re-charge apparatus is needed for prolonged, continuous reactions. Also, the immediate before

and after effects on the rate of the hydrogenation reaction can be observed as the added material is mixed with the Si mass bed. The reactor is designed to operate at pressures up to 500 psig which is the proposed operating pressure for the process-unit under development at Union Carbide.

2. Process Automation

The reactor design incorporates a number of automatic control devices into the hydrogenation apparatus. The idea is to automate the process to such a degree that the hydrogenation reaction can be left to run by itself up to 16 hours. Essentially, it allows the apparatus to operate over-night unattended. Naturally, precautionary measures are taken to safeguard an orderly shut down of the hydrogenation apparatus in the event of a general power failure or equipment malfunction. A number of safety devices are incorporated into the hydrogenation apparatus for this purpose. These safety devices will be discussed in Section (3). The process automation allows the hydrogenation experiment to run around the clock, 24 hours a day. Such a design feature is especially valuable for prolonged reactions designed to study the life of the Si mass bed. Severel hundred hours of reaction time can be conveniently accumulated. In contrast, a normal eight-hours-a-day operation provides six to seven hours of reaction time. Then, one has to shut down the reactor over-night and re-start again the next day. A continuous, 24 hours-a-day run will not only provide experimental data three times as fast, but also, it eliminates these undesirable inter-uptions.

Automatic $SiCl_4$ Feed

The automatic $SiCl_4$ feed system is schematically shown in Figure I. It includes a large cylinder for storing fresh $SiCl_4$, a $SiCl_4$ refill which contains the automatic operating mechanism (not shown in Figure I) and the $SiCl_4/H_2$ feed tank. The purpose of this design is to maintain a constant liquid level of $SiCl_4$ inside the $SiCl_4/H_2$ feed tank. The automatic feeding mechanism and the wiring diagram is shown in Figure III. A series of proximity switches are placed at various levels inside the immersion well in the $SiCl_4$ refill. These proximity switches can be actuated by a magnet which is attached to a float. One proximity switch is placed at the desired $SiCl_4$ liquid level for the $SiCl_4/H_2$ feed tank. A second proximity switch is placed at a slightly lower position. As $SiCl_4$ is consumed in the reaction, the liquid level falls until the float reaches the lower proximity switch. The attached magnet closes the proximity switch inside the immersion well. The closed electrical contact actuates a power relay. The power relay energizes the 4-way solenoid valve which applies air pressure to open the dual action, air-operated valve. The opened valve allows $SiCl_4$ to be pressure-fed into the $SiCl_4$ refill and the $SiCl_4/H_2$ feed tank. As the $SiCl_4$ liquid level rises, the float reaches the first proximity switch. The attached magnet actuates this proximity switch. The closed electrical contact energizes a second power relay as shown in Figure III. The power relay energizes the 4-way dual solenoid valve which exhausts air pressure

at the open position of the double acting, air-operated valve and, at the same time, applies air pressure to the close position of the air-operated valve to shut off the $SiCl_4$ flow. The process is repeated as $SiCl_4$ is consumed and the liquid level reaches the lower proximity switch again. The $SiCl_4$ liquid in the $SiCl_4/H_2$ feed tank is maintained at a constant level.

Storage Capacity for Starting Material

Sufficient storage capacities are provided to store the needed material for continuous operation of the hydrogenation apparatus. These include a large cylinder for $SiCl_4$ storage and a large receiver to hold the crude liquid chlorosilane product. A large Dry-Ice container provides sufficient cooling capacity for the -65 °C condenser to operate over-night. As for silicon metal, it is consumed slowly by the hydrogenation reaction at about 1% conversion per hour. Thus, the Si mass bed can be maintained at a constant level by intermittent manual addition of fresh Si metal into the reactor.

3. Operation Safety

The hydrogenation apparatus is fitted into a standard laboratory fume hood. This virtually eliminates the fire and explosion hazard due to the flammable hydrogen gas. It also safely exhausts corrosive chlorosilane vapors in case of an accidental spill. The safe operation of the hydrogenation apparatus is discussed in the following.

(a) The Nature of the Hydrogenation Reaction

The hydrogenation of $SiCl_4$ to $SiHCl_3$ in a mass bed of Si metal has been shown to be an equilibrium reaction. The reaction is only slightly exothermic to the extent of a few Kcal/mole of Si. The low heat of reaction plus the nature of the equilibrium virtually eliminate the possibility of a violent, run-away reaction. This is an advantage, not only from a process point of view, but also from a safety point of view.

(b) Pressure Rating Safety Factor

The entire hydrogenation apparatus is constructed of stainless steel. To obtain accurate reaction kinetic data, the reactor system must be totally leak-free. High quality Swagelok fittings are used throughout the apparatus. Instead of standard needle valves, Nupro bellows seal valves are used in places where high pressure applies at both sides of the valve under normal operating conditions. Swagelok fittings require a minimum wall thickness on the stainless steel tubings for a helium leak-free service. By virtue of this requirement, fairly heavy walled tubing is used. Consequently, the entire reactor system has a safe, nominal operating pressure in excess of 2,000 psig even though the hydrogenation reactor is designed to carry out experiments up to 500 psig reactor pressure. The 500 psig figure is the proposed reactor pressure for the process-unit under development at Union Carbide. Naturally, the hydrogenation apparatus will be leak-tested and pressure-tested before starting up the hydrogenation experiments.

(c) Automatic Shut Down Devices

The hydrogenation apparatus is semi-automated to allow the experiment to run by itself over-night unattended. Precautionary measures are carefully taken by incorporating a number of safety devices into the hydrogenation apparatus. These automatic shut-off devices ensure a safe shut down of the hydrogenation apparatus in case of the following plausible events,

(i) a general power failure with all utility to to the building shut off,

(ii) an over-pressure (plugging) or a under-pressure (leaks) condition develops in the hydrogenation apparatus,

(iii) a failure at the -65°C condenser system with no cooling to condense the chlorosilane products,

(iv) a malfunction develops at the automatic $SiCl_4$ feed system with no fresh $SiCl_4$ feed or the fresh $SiCl_4$ feed fails to shut off,

(v) a malfunction of the $SiCl_4/H_2$ feed to cause over-filling of the chlorosilane liquid product receiver,

(vi) an unforeseeable circumstance (e.g., a New England blizzard) prevents anyone from attending the hydrogenation experiment for more than 16 hours.

Once the safety shut down mechanism is triggered by one of these automatic shut down devices, the hydrogenation apparatus is put into a normal shut down mode which includes

(i) hydrogen gas shut off,

(ii) $SiCl_4$ feed shut off,

(iii) electrical power to the hydrogenation apparatus shut off.

The circuit diagram to automatically shut off electrical input to the hydrogenation apparatus is shown in Figure IV. All electrical power to the apparatus is controlled by power relays

which are constantly energized under normal operating conditions. If the power failure is of short duration (less than 3 minutes), all electrical equipment will be re-energized to resume normal operation as soon as electrical power to the building is restored. However, if the power failure is long-lasting, the hydrogenation experiment will be aborted by safety shutting down the apparatus. This is accomplished by a thermal relay which has a delay action of 3 minutes. The thermal relay is constantly energized under normal operating conditions. Power supply to the thermal relay is controlled by a high sensitiviy relay as shown in Figure IV. This normally closed high sensitivity relay cuts off power to the thermal relay when energized. As electric power to the thermal relay is cut off by a general power failure or by the action of the high sensitivity relay, the heater in the thermal relay starts to cool. The circuit is not effected as long as electrical power is stored within 3 minutes. However, when the failure condition persists for more than 3 minutes, the thermal relay turns itself off and permanently de-energizes the power relays which supply all the electrical power to the apparatus. Electrical power to the apparatus remains disconnected even though power to the building is restored. The thermal relay must be manually reset by the reset push button switch in Figure IV in order to re-connect electrical power to the hydrogenation apparatus.

To shut off the $SiCl_4$ feed, a normally open, air-operated valve is connected to the $SiCl_4$ feed line. Air pressure applied

to this air-operated valve is controlled by a 3-way solenoid valve. This solenoid valve is constantly energized under normal operating conditions. When a power failure occurs or when the 3-way solenoid valve is de-energized by the safe shut down mechanism, the de-energized, 3-way solenoid applies air pressure to the air-operated valve to shut off the $SiCl_4$ flow. The same principle can be applied to shut off the hydrogen gas feed to the apparatus. An air-operated valve is connected to the hydrogen feed line and it uses the same air pressure line which operates the air-operated valve for the safe $SiCl_4$ shut off. A separate cylinder of compressed air or nitrogen is used to supply air pressure to operate these safety shut off valves. This is a precautionary measure since a general power failure may shut off all utilities to the building; including air pressure.

To trigger a safe shut down of the hydrogenation reactor, a number of devices are incorporated into the hydrogenation apparatus. When activated by malfunctioning of the apparatus, these devices can: (1) apply electrical power to the high sensitivity relay in Figure IV to cause a 3 minute delay shut down, (2) energize another relay which cuts off electrical power to the apparatus and causes an immediate shut down with no delay. A Mercoid pressure switch is connected to the over-pressure alarm shown in Figure I. This pressure switch can be set to close electrical contacts at a pressure range, for example, 10% above and below the normal operating pressure. As malfunctions of the apparatus cause the reactor pressure to rise (plugging) or to

fall (leaking), the pressure switch closes and actuates the high sensitivity relay in Figure IV to shut down the apparatus. Similarly, a bimetallic thermal switch is incorporated into the cooling system for the -65°C condenser. This switch is set to close at rising temperature above -40°C. As cooling diminishes, the rising coolant temperature activates the bimetallic thermal switch to energize the high sensitivity relay to shut down the apparatus. The automatic $SiCl_4$ feed system uses proximity switches located inside the immersion well as shown in Figure IV. Additional proximity switches are placed above and below the normal operating range of the $SiCl_4$ liquid level. When the automatic $SiCl_4$ feed fails to charge fresh $SiCl_4$ into the $SiCl_4/H_2$ feed tank, the depleted $SiCl_4$ lowers the float to the position of the bottom proximity switch. The attached magnet in the float closes the bottom proximity switch and triggers the safe shut down mechanism. Similarly, failure of the automatic $SiCl_4$ feed to stop the $SiCl_4$ flow causes the $SiCl_4$ liquid level to rise to the position of the top proximity switch. The magnet attached to the float closes the top proximity switch and triggers the safe shut down mechanism. The same safety shut down device can be used for the chlorosilane liquid product receiver in Figure I. When the excessive chlorosilane crude exceeds the capacity of the receiver, the float rises to the top of the receiver. The attached magnet closes a proximity switch to trigger a safe shut down of the apparatus.

Finally, a 24 hour timer is connected to the automatic power shut off mechanism as shown in Figure IV. Before the hydrogenation experiment is left unattended for over-night operation,

the timer is set. The timer shuts off electrical power to the apparatus after 16 hours. It safely shut down the hydrogenation apparatus in the event that no one shows up for work the next day.

C. Summary of Progress

Experimental work on the hydrogenation studies has progressed on schedule according to the attached Program Plan. All essential equipment has been ordered. Construction and installation of the hydrogenation apparatus has begun. Shelf space for the instruments and a metal support structure for the hydrogenation apparatus were built. The control panel for variable transformers and switches has been completed. A constant temperature bath for heating the $SiCl_4/H_2$ feed tank has been constructed. A large Dry-Ice container for cooling the -65°C condenser has been built. The in-line gas chromatograph is completed. Fabrication of the reactor tube and installation of the reactor assembly are in progress. The hydrogenation apparatus is about 60% completed at the end of this first quarter.

PROJECTED SECOND QUARTER ACTIVITIES

Planned activities for the second quarter (July-October) include:

- complete construction and installation of the hydrogenation apparatus
- carrying out experiments on the hydrogenation of $SiCl_4$ to $SiHCl_3$
- collection of reaction kinetic data as a function of T, P, $H_2/SiCl_4$ ratio
- literature studies.

PROGRAM PLAN Investigation of the Hydrogenation of $SiCl_4$ (JPL Contract No. 955382)

Year	1979									1980												1981		
Month of Year	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3
Month of Contract	~~1~~	~~2~~	~~3~~	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
I Program Plan, Laboratory Site Preparation	~~1~~																							
II Finalize Reactor Design, Order Equipment	~~1~~	~~2~~																						
III Construct Hydrogenation Apparatus		~~2~~	~~3~~	4	5																			
IV Safety Review, Start-Up, Standardization				5																				
V Process Studies							▲						▲				▲							
A. Reaction Kinetics																								
(1) Function of T,P,$H_2/SiCl_4$: with no Catalyst				5	6	7	8																	
(2) Establish Rate Equation, Reaction Order							8	9																
(3) Copper Catalyst Studies: T,P,$H_2/SiCl_4$							8	9		10	11	12	13											
(4) Particle Size Distribution, Surface Area													13	14	15									
(5) Different Grade of MG Si														14	15	16								
B. Mass Life Studies																								
(1) With no Catalyst Added																	16	17	18					
(2) With Cu Catalyst Added																			18	19	20			
(3) Different Grade of MG Si																					20	21	22	
VI Research and Development							▲						▲				▲							
A. Method of Preparing Cu/Si Mass																								
(1) Literature Studies	~~1~~	~~2~~	~~3~~	4	5	6	7	8																
(2) Prepare Cu/Si Mass					5	6	7	8																
(3) Evaluation and Optimization							8	9		10	11	12	13											
B. Reaction Mechanism Studies																								
(1) Literature Studies	~~1~~	~~2~~	~~3~~	4	5	6	7	8																
(2) Identify Reaction Intermediates: HCl, etc.						6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21			
(3) Identify Intermediate Reaction Steps						6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21			
(4) Nature of the Equilibrium Reactions						6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21			
(5) The Role of Copper Catalyst																								
a. Nature of the Catalytic Sites							8	9		10	11	12	13	14	15									
b. Copper Transport Mechanism							8	9		10	11	12	13	14	15									
c. Copper Distribution on Solid Si Surfaces							8	9		10	11	12	13	14	15									
(6) Kinetic Isotope Effect													▲									22	23	
C. Other Hydrogenation Catalysts													▲									22	23	
VII Reports																								
A. Recomendation on Optimun Reaction Conditions									9					14					19				23	
B. Recomendation for Additional Development Work									9					14									23	
C. Final Report																							23	24

▲ Milestone Check Points

FIGURE 1 Apparatus For The Hydrogenation Of $SiCl_4$ To $SiHCl_3$

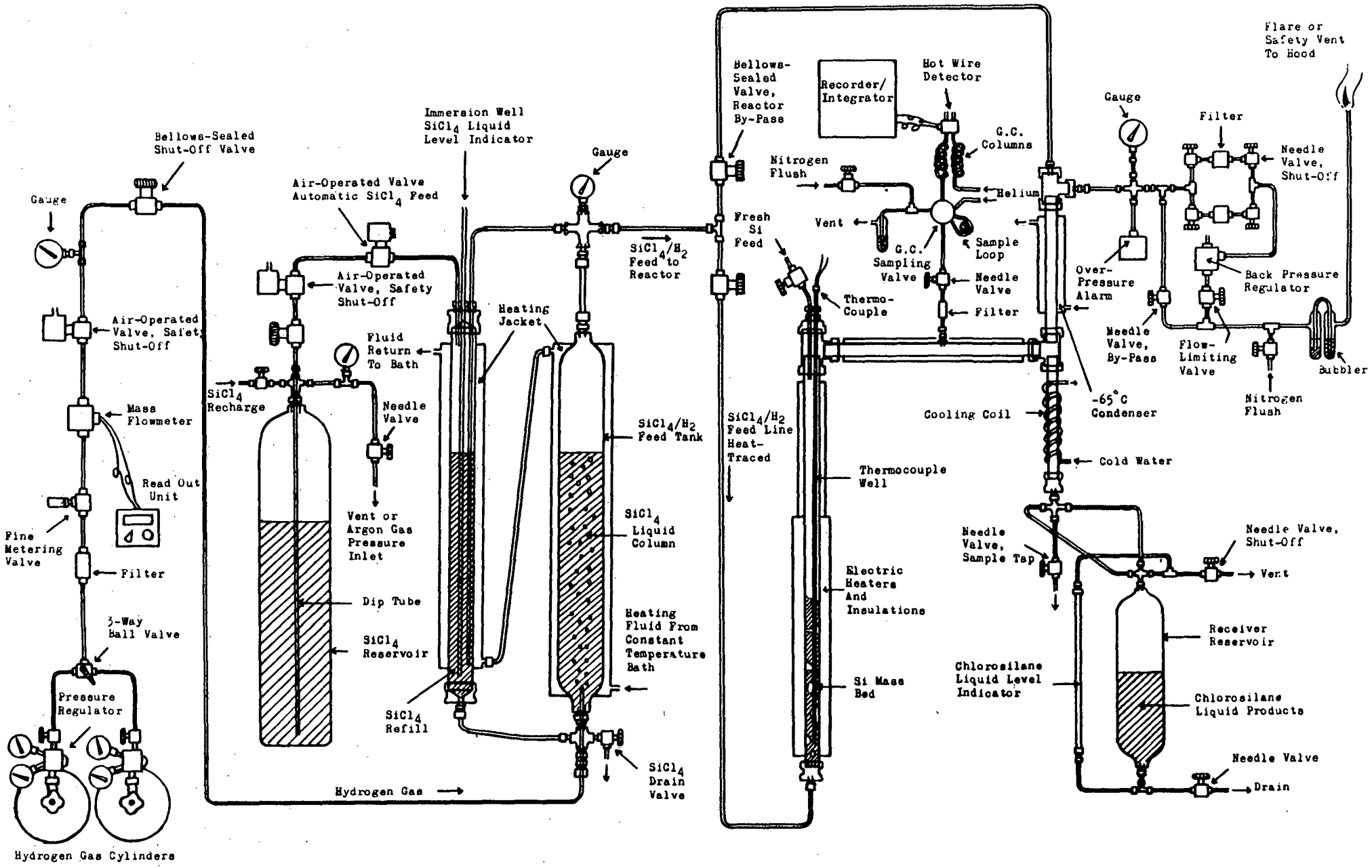


FIGURE II $H_2/SiCl_4$ Gaseous Inlet to Reactor and Grid Design

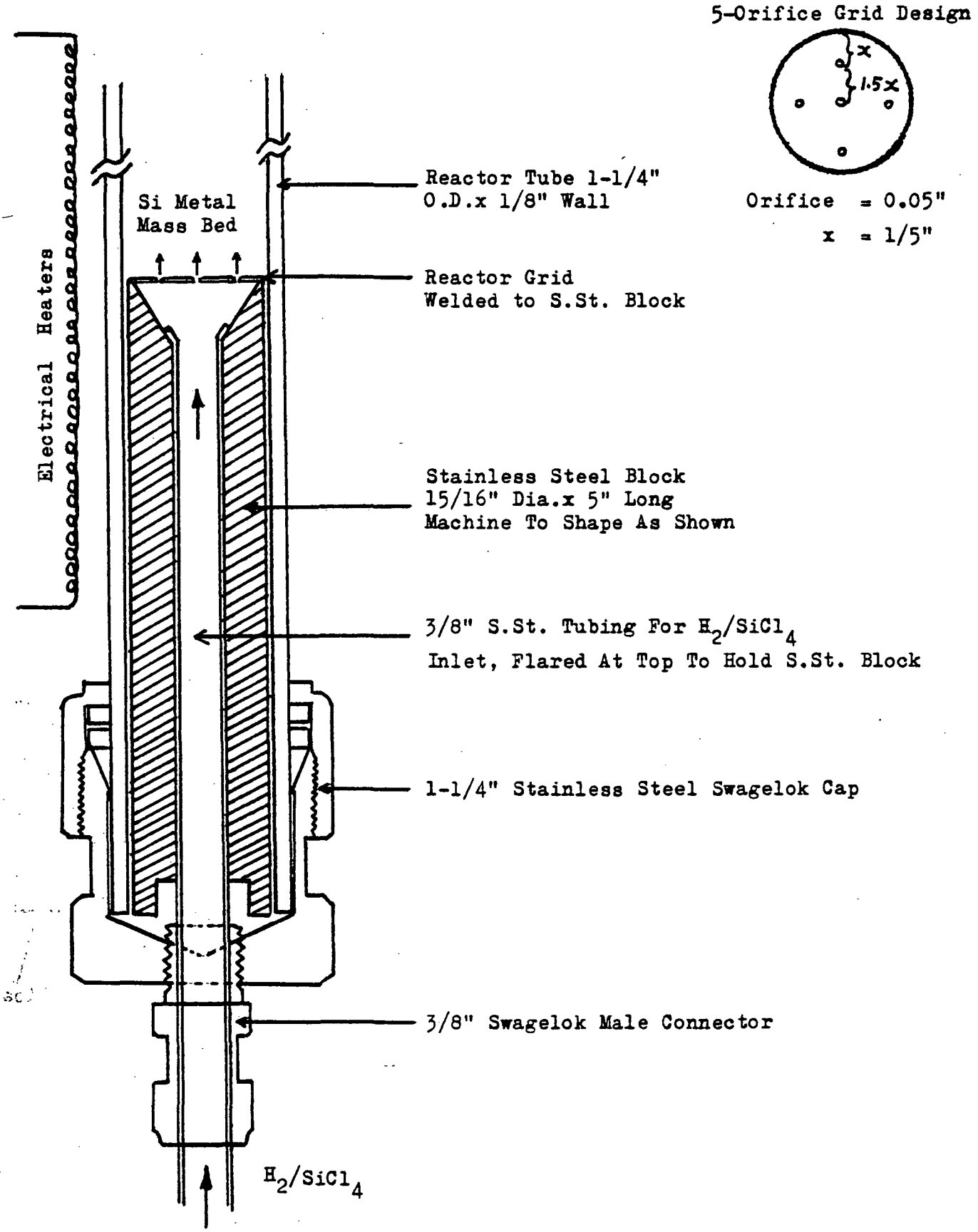


FIGURE III Automatic $SiCl_4$ Feed and Wiring Diagram

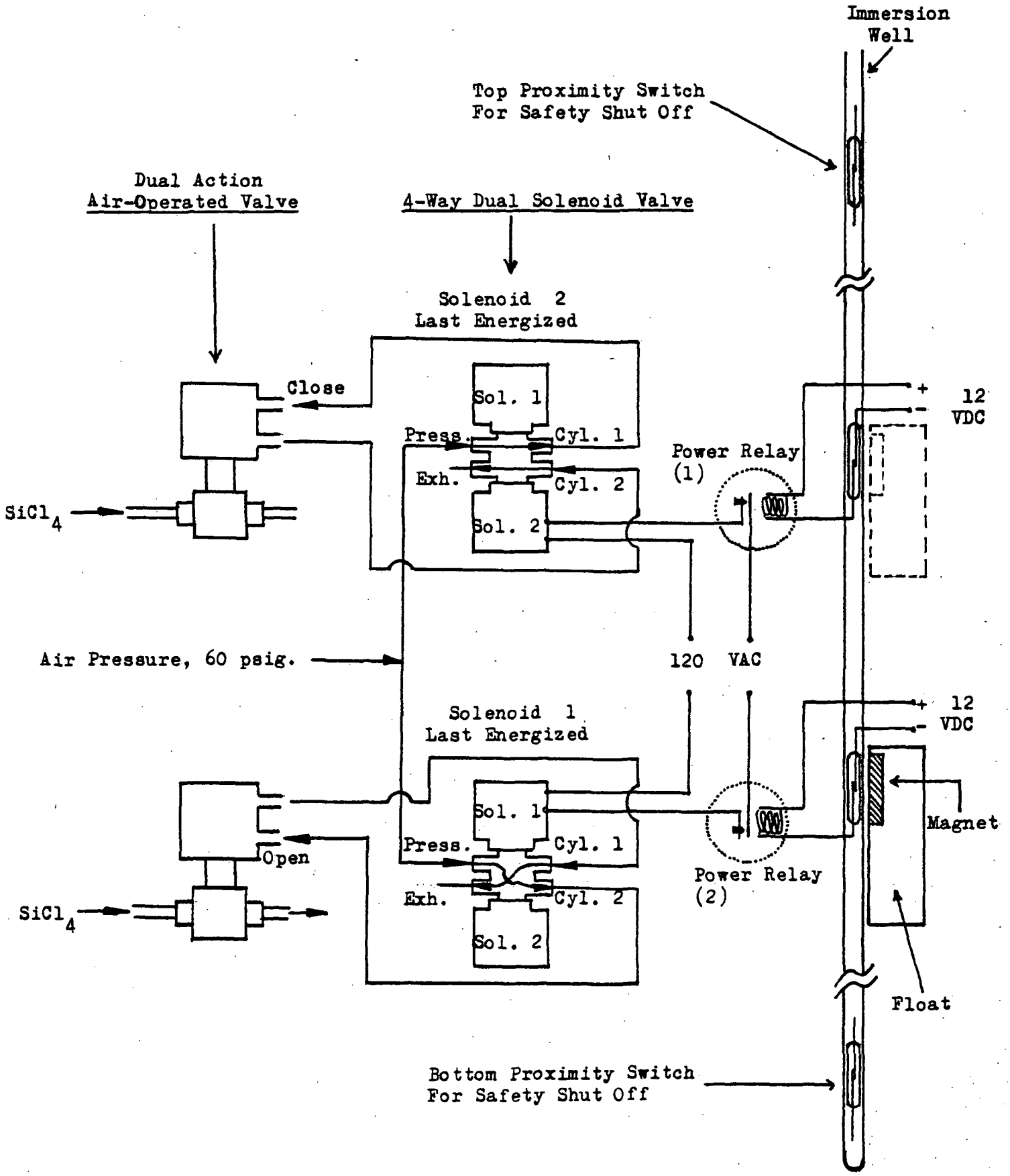
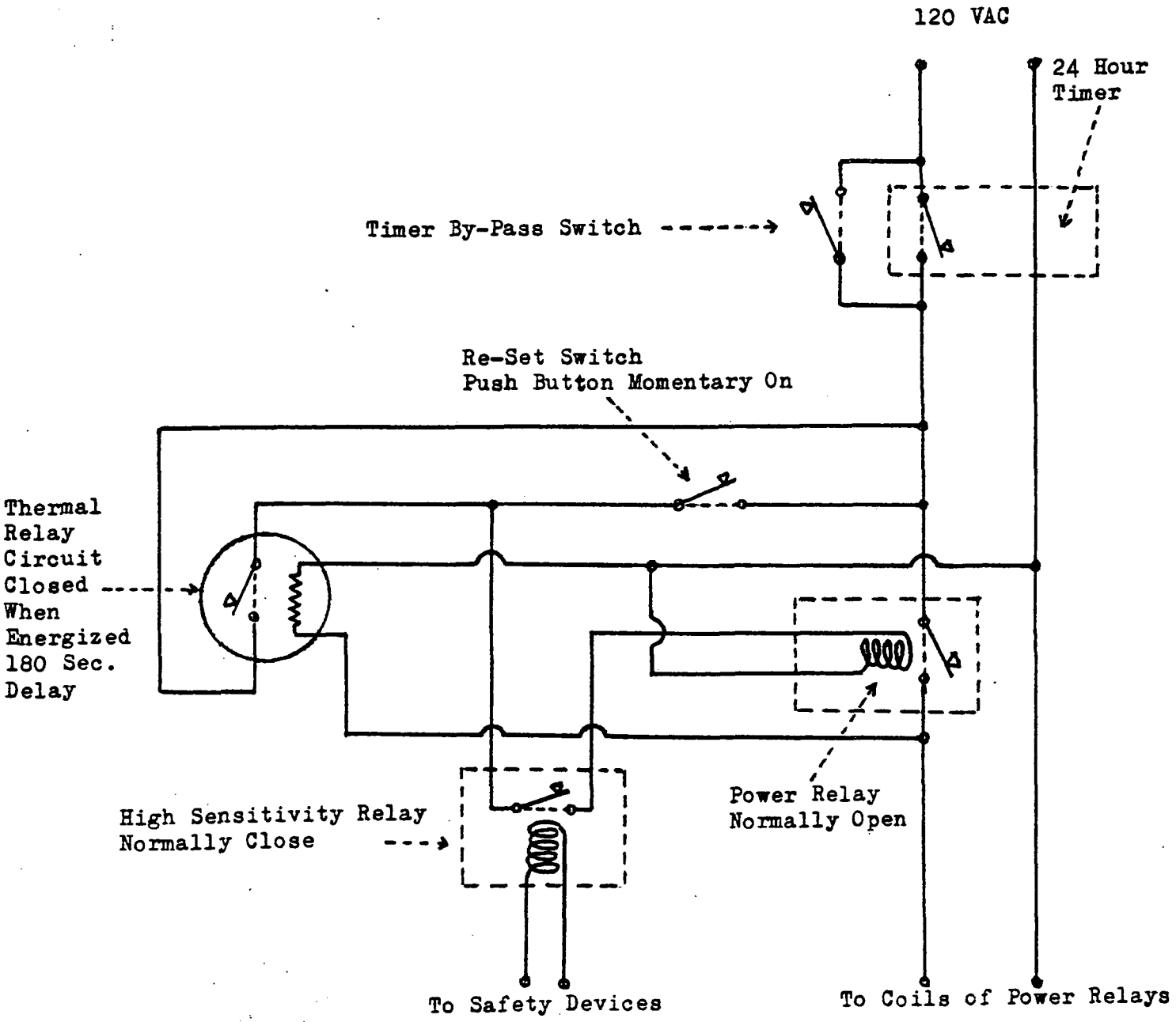


FIGURE IV Wiring Diagram for Automatic Shut Down


120 VAC
24 Hour Timer
Timer By-Pass Switch
Re-Set Switch
Push Button Momentary On
Thermal Relay Circuit Closed When Energized 180 Sec. Delay
High Sensitivity Relay Normally Close
Power Relay Normally Open
To Safety Devices
To Coils of Power Relays